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(54) Active electrode, electrochemical cell comprising the electrode and method of forming electrode

(57) Electrodes for use in an electrochemical system comprise a sulfide, selenide or telluride of a transition metal, copper, lead, or mixtures thereof. Electrochemical cells comprising the electrode and methods of forming the electrodes are also described.

GB 2 042 250 A

SPECIFICATION

Active electrode, electrochemical cell comprising the electrode and method of forming electrode

5 The present invention relates to novel active electrodes for redox systems such as S/S^{2-} , Se/Se^{2-} and Te/Te^{2-} , or mixtures thereof, to a process for the production of these and to cells containing such electrodes.

The use of electrocatalysts in polychalcogenide redox systems has hitherto received but little attention. Allen et al, Trans. Far. Soc. 53, 1626 (1957) studied the anodic oxidation of aqueous polysulphide on various electrode materials. Recently, photoelectrochemical cells based on polychalcogenides have aroused interest for the conversion of light into electricity, see US Patent No. 4,064,326, and Nozik: Ann. Rev. Phys. Chem. 1978.

10 It has become apparent that there exists a need for suitable counterelectrodes in such systems exhibiting a minimum of polarisation since polarisation reduces the power output of the cell and thus its efficiency. US Patent No. 4,064,326 discloses various metal sulphides which are good electrocatalysts for the polychalcogenide system. However, the preparation of such electrodes involves a number of steps some of which are moderately labour and energy intensive.

15 According to the present invention there are provided improved catalytically active electrodes for use in polychalcogenide redox systems which may preferably be S/S^{2-} and/or Te/Te^{2-} . The redox couples can be oxidised and reduced on the novel electrodes of the invention with very little polarisation. Such redox reactions can be effected at ambient temperature.

20 An electrode according to the invention for use in an electrochemical system comprises, as active material, a sulphide, selenide or telluride, or mixture of two or all of these, of one or more metals selected from transition metals, copper and lead. The preferred metals are cobalt, nickel, copper, lead, molybdenum and ruthenium.

25 Preferred active materials have the approximate formulae CoS , Cu_2S , $PbSe$, RuS_2 , MoS_2 , $NiTe$, and Cu_2Se . The materials may have the exact formulae or materials differing within a wide range of stoichiometric ratios may be used. This applies particularly to copper polychalcogenides. Materials such as $Cu_{1.75}S$ are very effective electrocatalysts.

30 The invention includes also electrochemical cells comprising the electrodes and generally also a polychalcogenide electrolyte.

The electrodes find special use in photoelectro-chemical cells where problems of losses due to polarisation are to be overcome. They are advantageously used as counterelectrodes (i.e. additional electrodes besides the anode and cathode) in electrochemical cells wherein polychalcogenide solutions improve cell performance and stability.

35 The novel electrodes are superior to electrodes hitherto described as well as being less expensive in some cases and being relatively simple to manufacture.

The catalytic material in the electrodes according to the invention has good electrical conductivity and good mechanical stability in the systems in which they are used. They are fully or adequately chemically stable in the systems, to the extent that although some may undergo chemical exchange with the electrolyte this must occur without substantial deleterious effects.

40 The active material is generally supported on a support that is chemically inert in the system.

The substrate or support which is chemically inert in the system in the bulk state can be selected from the group comprising steel, stainless steel, porous carbon, graphite, cobalt, titanium, tantalum, tungsten, vanadium or chromium. The electrode may comprise a metal or metal alloy body that provides a support matrix that is chemically inert to the electrochemical system and that carries a surface layer of the chosen active material. Thus an alloy may contain an element that will serve as a catalyst or a precursor of a catalyst and another element which serves as a matrix for the catalyst or precursor. For instance in the sulphidisation of brass, the starting material is its own support (in this case, brass metal). The reason for using alloys in this type of electrode - Cu-Zn instead of pure Cu, which is initially more active - is that copper is dimensionally unstable in chalcogenide electrolytes, and gradually disintegrates. By adding increasing amounts of a matrix metal, e.g. zinc, the dimensional stability increases. It should be noted, that besides commercially available alloys (such as brass) other Cu-containing alloys may be used, as long as the other components of the alloy have no deleterious effects on electrode performance. Such alloys can be prepared conveniently by alloy plating on, for example, a stainless steel support, thus greatly decreasing the amount of alloy elements needed.

55 The invention also includes processes for making electrodes for use in an electrochemical system containing at least one polychalcogenide redox couple comprising forming an active layer of a sulphide, selenide, telluride or mixture thereof on a support, and in particular includes processes for making electrodes as described above comprising forming a layer of the said active material on a support.

60 The method may involve forming a layer of the active material or a precursor on the support by electrolysis and, if necessary, converting the precursor to the active material.

In one method of the invention, a layer is formed of a hydroxide precursor of the active material and this is converted to a sulphide, selenide, telluride or mixture thereof. In another method a layer is formed of a metal oxide or hydrated metal oxide and this is converted to a sulphide, selenide, telluride or mixture thereof. In another method a high surface area layer of metal is formed on the support and the metal is converted to the

sulphid, selenide, tellurid or mixture thereof.

Instead of depositing the layer of active material or precursor by electrolysis other methods can be used. For instance it can be deposited by dipping, sputtering, chemical vapour deposition or spraying or part or all of the support, or at least the surface of the support, may be a precursor of the active material and may be converted at the surface to form the active material.

It should be noted that the activity of the electrocatalytic electrodes of the invention is strongly dependent on the electrolyte composition and the temperature of the electrolyte. As in any normal electrochemical system, the activity increases with increase in temperature and increase of the concentration of electroactive species (the reduced form of the chalcogenide, e.g. S^{2-} for the anodic process, and oxidized form for the cathodic process). However, if the ratio of the oxidized to the reduced form exceeds unity, i.e., $X/X^{2-} > 1$, the activity drops, for both cathodic and anodic processes, the drop increasing as the ratio increases. In short, the optimum concentration is a maximum concentration of electroactive species, but with the ratio $X/X^{2-} \leq 1$. According to a preferred embodiment, use is made of an electrolyte composition $[OH^-] = 1$; $[X^{2-}] = 1$; $[X] = 1$. This is close to the optimum composition for the counterelectrode. A composition of $[OH^-] = 2$; $[X^{2-}] = 2$; $[X] = 2$ to M is even somewhat better, although the difference is not very pronounced.

The invention is illustrated with reference to the following nonrestrictive Examples.

Example 1: Cobalt Sulfide on Stainless Steel

A dilute solution of a Co^{2+} salt buffered to a pH between 3 and 7 is used as the electroplating solution. A stainless steel substrate serves as the cathode and cobalt metal is used as the anode, one anode is provided on each side of the cathode to improve current distribution and to give a more even layer on both sides of the substrate. The conditions of electrolysis may vary. The electrolyte contained 20g $CoSO_4$ /litre buffered to pH=4.5 with potassium biphthalate and NaOH. The electrolysis was carried out at room temperature, without stirring and at a current of about 40 mA/cm² of substrate area during 5 minutes. The lower the pH, the greater the current density required. Too low a current density, below about 20 mA/cm², or too low a pH, below about pH 3, leads to a layer rich in Co metal which is less active than the $Co(OH)_2$ which is plated under optimum conditions.

The plated layer is immersed in a chalcogenide ion electrolyte and converted to CoX ; e.g. in S^{2-} containing solution, CoS is formed. An electrolytic reduction at about -1.2 V with respect to Standard Calomel Electrode improves the performance. Under standard conditions (30°C; 1M KOH, 1M $Na_2S \cdot 9H_2O$, 1M S) such an electrode gives 8 mA/cm² at a polarization of 10mV, and follows a linear behaviour, at least to beyond 60 mA/cm² in both cathodic and anodic directions, i.e. 16 mA/cm² for 20 mV polarization, etc. When a thicker layer is plated, the electrode is more active, but is mechanically less stable.

Example 2: $Pb_{0.9}Se_{0.1}$ on Stainless Steel

A layer of PbO_2 is plated onto a steel substrate by anodic deposition from a 0.3M aqueous solution of lead acetate or nitrate, using a Pt cathode. The plating is carried out at 40 mA/cm² at room temperature for 5 minutes, to form a dark red-brown layer of about 10 microns thick. This electrode is then reduced in a polychalcogenide solution under the same conditions as for CoS in Example 1. In this instance reduction is a necessity. In an electrolyte of 1M S^{2-} , 0.9M S and 0.1M Se, a mixed lead sulphide/selenide is formed, which in the same electrolyte gives 7.5 mA/cm² at a polarization of 10mV and show a linear I-V behavior in both directions up to at least 60 mA/cm².

Example 3: Cu_2S in an Alloy Matrix

Brass gauze (66% Cu, 34% Zn, 70 mesh) is immersed in a 1M S; 1M S^{2-} and 1M OH^- polysulfide solution which can be the polysulfide (or polychalcogenide) electrolyte in which the electrode is to be used. The brass blackens over the course of several days indicating sulfidization of the copper present in the brass. The process can be accelerated by anodizing the brass in the polysulfide electrolyte at a potential of +0.5 to 1.0 V versus Standard Calomel Electrode, in which case the process takes only about 5 minutes. An electrode prepared in this manner gives 25.5 mA at 10mV polarization for a 3 cm² electrode, i.e., 8.5 mA/cm², when immersed in a solution 1M each in KOH, $Na_2S \cdot 9H_2O$ and S, at 30°C. It shows a linear I-V behaviour up to at least 70 mA/cm² in both directions. The brass gauze can contain from 60 to nearly 90 mole percent of Cu, being composed of gauze from 30 to 150 mesh, without substantially changing the performance.

Example 4: Alloy Plating of Cu-containing Alloy, and Sulfidization

A solution containing 4 grams $CuCN$, 1.2 g $Zn(CN)_2$ and 6.5 grams NaCN in 100 ml H_2O is prepared. A piece of stainless steel is cleaned thoroughly and degreased by washing in trichloroethylene. As in Example 1, the stainless steel is connected as the cathode to a composite anode of copper and of zinc with an area ratio of 9 Cu:1 Zn. A current of 6 mA, per cm² of stainless steel substrate, is passed for 30 minutes at about 40°C. The electrode, so obtained is used, without further treatment, in a chalcogenide solution.

Under the standard conditions of Example 1 such an electrode gives 10 mA/cm² at a polarization of 10mV, and behaves linearly up to > 80 mA/cm².

Example 5: CoS on Steel

Equivalent solutions of cobalt acetate and KOH were rapidly mixed, yielding a green precipitate.

A 4 cm² sheet of 0.7 mm thick stainless steel is cleaned thoroughly by sand blasting. The green precipitate is painted onto the substrate by means of a paintbrush. After letting the painted substrate dry in air under ambient conditions, a second layer is painted on top of the first one. After drying, the electrode is immersed into an aqueous solution 1M each in KOH, Na₂S.9H₂O and S. The electrode is reduced in this solution at a potential 1.2V negative with respect to Standard Calomel Electrode for 5 minutes. After reduction this electrode shows a polarization of up to 20mV at a current density of 10 mA/cm² (40 mA). It is relatively stable in air; however prolonged contact with oxygen should be avoided.

Example 6: RuS₂ Electrodes

An aqueous solution was prepared of 5 mg RuCl₃ in 10 ml H₂O. A 1 cm² smooth piece of platinum is used as the anode and a piece of steel 1 cm² on each side is the cathode. The electroplating is performed at currents up to 60mA (30 mA/cm²) for 10 minutes. The electrode is now transferred to a solution containing 1M of S, of Na₂S.9H₂O and of KOH and is found to polarize up to 90 mV at current densities of 10 mA/cm². When the electrode is now reduced at about 1V negative to Standard Calomel Electrode a polarization of 48 mV for the same current density is found.

Example 7: Ni-Sulfide on Stainless Steel

A Solution is prepared containing 4 gm nickel ammonium sulphate per 1 liter H₂O. (Alternatively a solution like the one described in Example 1 but with NiSO₄ instead of CoSO₄ can be used). The electrolysis conditions are those described in Example 1: The plated layer is immersed in a solution 1M each in KOH, Na₂S.9H₂O and S and is polarised at 10mV when a current of 5.8 mA/cm² is passed and follows a linear I-V behaviour up to about 50 mA/cm².

Example 8: Ni-Selenide Electrode

An electrode is prepared as in Example 7. The plated layer is immersed in a solution of 3M KOH, 0.3M Se and 0.3M selenide. After reduction at 30 mA/cm² for 5 minutes, this electrode shows a 10mV polarization when a current of 2.4 mA/cm² is passed. Under standard conditions (Example 1) such an electrode shows a 10mV polarization, when a current of 4.8 mA/cm² is passed.

Example 9: NiSe_{0.8}Te_{0.2} Electrode

An electrode is prepared as in Example 7. The plated layer is immersed in a solution of 2M KOH, 0.25M Se, 0.05M Te, and 0.25M selenide. After reduction at 20 mA/cm² for 5 minutes the electrode is polarized at 10mV when a current of 4.5 mA/cm² is passed. Under standard conditions (Example 1) a current of 5.5 mA/cm² gave rise to 10 mV polarization.

Example 10: Cobalt-Telluride Electrode

An electrode is prepared as in Example 1 and reduced in a telluride solution (0.1M Te, 0.1MTe, 4M KOH). After reduction for 5 minutes at 15 mA/cm² the electrode is polarized at 20 mV when a current of 7 mA/cm² is passed. Under standard conditions in a polysulphide solution, such as that of Example 1, a current of 6 mA/cm² gives rise to 10 mV polarization.

Example 11: CoSe_{0.8}Te_{0.2} Electrode

An electrode is prepared as in Example 1 and reduced in a telluride-selenide solution of Example 9 for 5 minutes at 20 mA/cm². A current of 5 mA/cm² gives rise to 10mV polarization in this solution, and 6 mV polarization in a standard solution of Example 1.

Example 12: Lead Telluride Electrode

An electrode is prepared as in Example 2 and reduced in a telluride solution as in Example 10 for 5 minutes at 15 mA/cm². This electrode is polarized by 24 mV when a current of 7 mA/cm² is passed. Under standard conditions of Example 1 the current is 5.8 mA/cm² at a polarization of 10 mV.

Example 13: Lead-Selenide-Telluride Electrode

An electrode is prepared as in Example 2 and reduced in a telluride-selenide solution of Example 9 for 5 minutes at 20 mA/cm². The electrode is polarized by 10mV when a current of 4.0 mA/cm² is passed. Under standard conditions of Example 1 the current is 5.7 mA/cm² at the same polarization.

Example 14: Molybdenum Sulfide Electrode

A MoS₂ electrode on molybdenum metal is prepared by painting a slurry of molycote (Climax Molybdenum) in ethylene glycol on molybdenum, drying in air and heating for 10 minutes at 450°C in air. Under standard conditions of Example 1 the electrode is polarized to 10 mV when a current of 1 mA/cm² is passed.

The following Table illustrates electrodes according to the invention, their mode of preparation, catalytic activity and the electrolyte in which activity is measured. As a measure of catalytic activity, the polarization is given (in mV) for a current of 10 mA at an electrode of 1 cm² geometric area, covered on both sides with electrocatalyst. The smaller the polarization, the more active the electrocatalyst. As the I-V behavior around

the redox potential is linear, these values apply to both the cathodic and anodic directions.

TABLE

Electrode Material	Type of Preparation	Activity (mV)	Solution (30°) OH/X ²⁺ /X (X=S, except when noted)
CoS	Painting with Co(OH) ₂ gel	15.0	1/1/1
NiSe	Electroplating Ni(OH) ₂	43.0	3/3Se ²⁻ /3Se
Cu ₂ S	<i>In situ</i> sulfidization of high brass	15.0	1/1/1
CoS	Electroplating Co(OH) ₂	14.0	1/1/1
Cu ₂ S	Precipitation of Cu ₂ S in carbon	11.0	1/1/1
PbTe	Electroplating PbO ₂ and reduction in Te ²⁺ X solution	40.0	1/1/1
PbSO ₄ SeO ₃	Electroplating PbO ₂ and reduction in S ₂ Se ²⁻ -O.11 solution	13.0	1/1/1
RuS ₂	Electroplating	48.0	1/1/1
MoS ₂	Painting of MoS ₂ on Mo	75.0	1/1/1
Platinized Pt	Electroplating	110	1/1/1
(for comparison)			

CLAIMS

1. An electrode for use in an electrochemical system and comprising as active material a sulphide, selenide or telluride or mixture of two or all of these of one or more metals selected from transition metals, copper and lead.
2. An electrode according to claim 1 in which the one or more metals are selected from cobalt, nickel, molybdenum, ruthenium, copper and lead.
3. An electrode according to claim 2 comprising an active material selected from compounds having the approximate formulae CoS, Cu₂S, PbSe, RuS₂, MoS₂, NiTe and Cu₂Se.
4. An electrode according to any preceding claim comprising a high surface area of the active material.
5. An electrode according to any preceding claim in which the active material is supported on a support that is chemically inert to the electrochemical system.
6. An electrode according to claim 5 in which the support is selected from steel, stainless steel, porous carbon, graphite, cobalt, titanium, tantalum, tungsten, vanadium and chromium.
7. An electrode according to claim 5 or claim 6 comprising a metal or metal alloy body that provides a support matrix that is chemically inert to the electrochemical system and that carries a surface layer of the said active material.
8. An electrode according to claim 7 comprising brass carrying a surface layer comprising a sulphide, selenide or telluride, or mixture of two or all of these, of copper.
9. An electrode according to claim 1 substantially as herein described with reference to any of the examples.
10. An electrochemical cell comprising an electrode according to any preceding claim.
11. A cell according to claim 10 and which is a photoelectrochemical cell.
12. A cell according to claim 11 in which the electrode according to any of claims 1 to 9 is a counterelectrode.
13. A cell according to any of claims 10 to 12 including a chalcogenide electrolyte.
14. A process for making an electrode according to any of claims 5 to 8 comprising forming a layer of the said active material on the support.
15. A process for making an electrode for use in an electrochemical system containing at least one polychalcogenide redox couple, the method comprising forming on a support an active layer of sulphide, selenide, telluride or mixture of two or three of these.
16. A process according to claim 14 or claim 15 comprising forming a layer of the said active material or a precursor on the support by electrolysis, and if necessary, converting the precursor to the active material.
17. A process according to any of claims 14 to 16 comprising forming a layer of a hydroxide precursor of

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the active material and converting it to the sulphide, selenide, telluride or mixture of two or all of these.

18. A process according to claim 14 or claim 15 comprising forming a layer of an oxide or hydrated oxide precursor of the active material and converting it to the sulphide, selenide, telluride or mixture of two or all of these.

5 19. A process according to claim 14 or claim 15 comprising forming a high surface area metal layer and converting the metal to the sulphide, selenide, telluride or mixture of two or all of these.

20. A process according to claim 14 or claim 15 substantially as herein described with reference to any of the examples.

21. An electrode made by a process according to any of claims 14 to 20.

10

New claims or amendments to claims filed on 23 April 80

Superseded claims 6, 7, 14 to 19

New or amended claims:-

15 6. An electrode according to claim 5 in which the support is selected from steel, stainless steel, carbon, graphite, cobalt, titanium, tantalum, tungsten, vanadium and chromium.

7. An electrode according to claim 5 or claim 6 comprising a metal or metal alloy body that provides a support matrix that is chemically inert to the electrochemical system and that carries a surface of the said active material.

20 14. A process for making an electrode according to any of claims 5 to 8 comprising forming a surface of the said active material on the support.

15. A process for making an electrode for use in an electrochemical system containing at least one polychalcogenide redox couple, the method comprising forming on a support on active surface of sulphide, selenide, telluride or mixture of two or three of these.

25 16. A process according to claim 14 or claim 15 comprising forming a surface of the said active material or a precursor on the support by electrolysis, and if necessary, converting the precursor to the active material.

17. A process according to any of claims 14 to 16 comprising forming a surface of a hydroxide precursor of the active material and converting it to the sulphide, selenide, telluride or mixture of two or all of these.

30 18. A process according to claim 14 or claim 15 comprising forming a surface of an oxide or hydrated oxide precursor of the active material and converting it to the sulphide, selenide, telluride or mixture of two or all of these.

19. A process according to claim 14 or claim 15 comprising forming a high surface area metal surface and converting the metal to the sulphide, selenide, telluride or mixture of two or all of these.

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